TEST REPORT T71-6-1

QUALITATIVE ANALYSIS OF PRIMERS, TRACERS, IGNITERS, INCENDIARIES, BOOSTERS, AND DELAY COMPOSITIONS ON A MICRO SCALE BY USE OF INFRARED SPECTROSCOPY

by

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June 1971

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DEPARTMENT OF THE ARMY
FRANKFORD ARSENAL
Philadelphia, Pa. 19137

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13. ABSTRACT

The application of infrared spectroscopy to the detection of the constituents of primers, tracers, igniters, incendiaries, boosters, and delay compositions on a micro scale was investigated. It is shown that these constituents can be identified quickly and with certainty, using infrared pellet technique to detect organic and inorganic compounds and emission spectroscopy to identify the metals. In making the pellet, 1 to 2 mg of the material is ground with 300 mg of potassium bromide and the pellet formed in the die press. The grinding and pressing operation has been found to be completely safe even with the most sensitive explosives, once the material has been mixed with the potassium bromide. The infrared spectra of 43 of the most common ingredients of primers, tracers, igniters, incendiaries, boosters, and delay compositions are given over the range 2.5 to 50 microns. The qualitative analysis of seven typical compositions is demonstrated.

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I. SUMMARY

The application of infrared spectroscopy to the detection of the constituents of primers, tracers, igniters, incendiaries, boosters, and delay compositions on a micro scale was investigated. It is shown that these constituents can be identified quickly and with certainty, using infrared pellet technique to detect organic and inorganic compounds and emission spectroscopy to identify the metals. In making the pellet, 1 to 2 mg of the material is ground with 300 mg of potassium bromide and the pellet formed in the die press. The grinding and pressing operation has been found to be completely safe even with the most sensitive explosives, once the material has been mixed with the potassium bromide. The infrared spectra of 43 of the most common ingredients of primers, tracers, igniters, incendiaries, boosters, and delay compositions are given over the range 2.5 to 50 microns. The qualitative analysis of seven typical compositions is demonstrated.

II. RECOMMENDATIONS

It is recommended that the methods and spectra described in this report be included in MIL-STD-650 (Military Standard, Explosive: Sampling, Inspection and Testing).

III. INTRODUCTION

The constituents of primers, tracers, igniters, incendiaries, boosters, and delay compositions are ordinarily identified by wet chemical tests for the organic compounds, anions, and metals (frequently emission spectrography is used for the metals). These wet tests are often untrustworthy, especially if applied on a micro scale.

This laboratory undertook an investigation on the application of infrared spectroscopy to the detection of the organic compounds and inorganic compounds present in primers, tracers, igniters, incendiaries, boosters, and delay compositions. It was believed that such an infrared technique together with emission spectroscopy (for inorganic materials that do not give infrared spectra) would provide an excellent means for the qualitative analysis of the constituents in question.

Pristera and Fredericks (3) have compiled spectra of most constituents of propellants and explosives. However, their compendium does not include many of the very sensitive explosive compounds found in primers, tracers, igniters, incendiaries, boosters, and delay compositions and it does not include the far infrared. Miller et al (1, 2) have compiled spectra of inorganic compounds but their collection does not include many of the inorganic compounds found in primers, tracers, igniters, incendiaries, boosters, and delay compositions. Pristera and Fredericks (3) and Miller et al (1, 2) used a prism type infrared spectrophotometer; the present authors used a grating type.

IV. STUDY

A. RECOMMENDED METHOD FOR PREPARATION OF SPECTRA

1. Apparatus and Reagents

Perkin-Elmer Model 621 Infrared Spectrophotometer.

Evacuable potassium bromide die (Model 186-0025, Perkin-Elmer Corp., Norwalk, Conn).

Adapters for mounting KBr discs on spectrophotometer.

Twenty-ton hydraulic press.

Vacuum pump.

Mortars (o.d. 50 mm) with pestles.

Plastic microspatula.

Potassium bromide, infrared grade (Harshaw Chemical Co., Cleveland, Ohio).

2. Preparation of Potassium Bromide Pellets

Grind 1 - 2 grams of infrared grade KBr (in small portions) and store in a desiccator until needed.

Add 1 - 2 mg of sample to the mortar with a plastic microspatula (this is most conveniently done by first taring the mortar). Weigh 300 mg of the preground KBr into an aluminum balance pan and add all the KBr to the mortar. Using the plastic microspatula, thoroughly mix the KBr with the sample. Grind the sample-KBr mix for about three minutes. Scrape the sample-KBr mix loose from the mortar surface with the plastic microspatula and transfer it to the die. Level the sample-KBr mix with the microspatula and insert the plunger. Evacuate the die for three minutes with a vacuum pump without applying pressure, then apply 18,000 pounds pressure with a hydraulic press for five minutes.

Disassemble the die and push out the KBr pellet with a gentle application of the hydraulic press. Mount the pellet on an adapter and scan the spectrum from 2.5 to 50 microns with a blank KBr pellet in the reference beam. Use a dry air purge for the far infrared region (30 to 50 microns). The following settings were used on the Perkin-Elmer Model 621 infrared spectrophotometer: slit program, 1000; gain 5.1; attenuator speed, 1100; scan drive, 1; scan time, 16; supression, 8; scale, 1x; source current, 0.8.

B. RESULTS AND DISCUSSION

The spectra obtained for the 43 commonly used ingredients of primers, tracers, igniters, incendiaries, boosters, and delay compositions are shown in Figures 1 to 43. These ingredients are arranged (Table I) according to function as follows: primary explosives, high explosives, oxidizers, color intensifiers, binders, and miscellaneous. Compounds having more than one usage are listed according to their major function; for example, polyvinyl chloride is used as a binder or color intensifier but is listed under binders. Lead thiocyanate, the only fuel that gives a spectrum, is listed under miscellaneous; other fuels (magnesium, aluminum, zirconium, titanium, boron, silicon, and metallic hydrides) do not give infrared spectra.

The spectra of seven typical explosive compositions together with the notation of the peaks identifying the principle constituents are shown in Figures 44 to 50. The conclusions concerning the analysis of these compositions drawn from these spectra and the emission spectrographic analysis are shown in Table II.

It is seen that normal lead styphnate can be distinguished from basic lead styphnate by infrared. The different oxides of lead, iron, and barium may also be distinguished (PbO, Pb_3O_4, Fe_2O_3, BaO, and BaO_2 give unique spectra, while PbO and Fe_3O give no spectra).

In some spectra there is evidence of light scattering in the high frequency end of the spectrum. This is caused by inadequate grinding or the presence of such ingredients as antimony sulfide, magnesium, aluminum or zirconium. However, in no instance was the problem severe enough to interfere with the qualitative use of the spectrum.

The majority of spectra indicated the presence of small amounts of moisture; hence, care must be taken to avoid misinterpreting peaks occurring in the regions of 3420 cm^{-1} and 1630 cm^{-1}.

A special concentration procedure must be used to detect tetracene (2 to 4%) present in some lead styphnate primers. In this concentration procedure, about 50 mg of the primer contained in a sintered glass crucible is washed successively with ammonium acetate solution (20%), water, and acetone to remove lead styphnate, barium nitrate, and PETN. About 3 or 4 mg of the residue, which contains the tetracene and antimony sulfide is then used for the pellet.

It might be thought that preparing potassium bromide pellets from very sensitive explosive materials would be hazardous. This did not prove to be the case for the following reasons: (a) a very small amount of the explosive is used, (b) the potassium bromide acts as a diluent.

In the emission spectrographic analysis of explosives, it is customary in this laboratory to first destroy the explosive by treatment with concentrated nitric acid and evaporation to dryness.

V. BIBLIOGRAPHY

(1) Miller, F. A., Carlson, G. L., Bently, F. F., and Jones, W. H., Spectrochim. Acta, 16, 135 (1960).

(2) Miller, F. A., and Wilkens, C. H., Anal. Chem., 24, 1253 (1952).

(3) Pristera, F., and Fredricks, W., Picatinny Arsenal Technical Memorandum 1887, September 1969.

VI. TABLES

Table I. Identification of Spectra

	Spectrum	Code
1.	Lead azide	Primary Explosive 1
2.	Mercury fulminate	Primary Explosive 2
3.	Tetracene	Primary Explosive 3
4.	Normal lead styphnate	Primary Explosive 4
5.	Basic lead styphnate	Primary Explosive 5
6.	RDX (cycotrimethylenetrinitramine)	High Explosive 1
7.	HMX (cyclotetramethylenetetranitramine)	High Explosive 2
8.	Tetryl (2,4,6-trinitrophenylmethylnitramine)	High Explosive 3
9.	PETN (pentaerythrite tetranitrate)	High Explosive 4
10.	TNT (2,4,6-trinitrotoluene)	High Explosive 5
11.	Nitrocellulose	High Explosive 6
12.	Styphnic acid	High Explosive 7
13.	Ammonium nitrate	Oxidizer 1
14.	Sodium nitrate	Oxidizer 2
15.	Potassium nitrate	Oxidizer 3
16.	Barium nitrate	Oxidizer 4
17.	Strontium nitrate	Oxidizer 5
18.	Lead nitrate	Oxidizer 6
19.	Potassium chlorate	Oxidizer 7
20.	Ammonium perchlorate	Oxidizer 8

Table I. Identification of Spectra (cont'd)

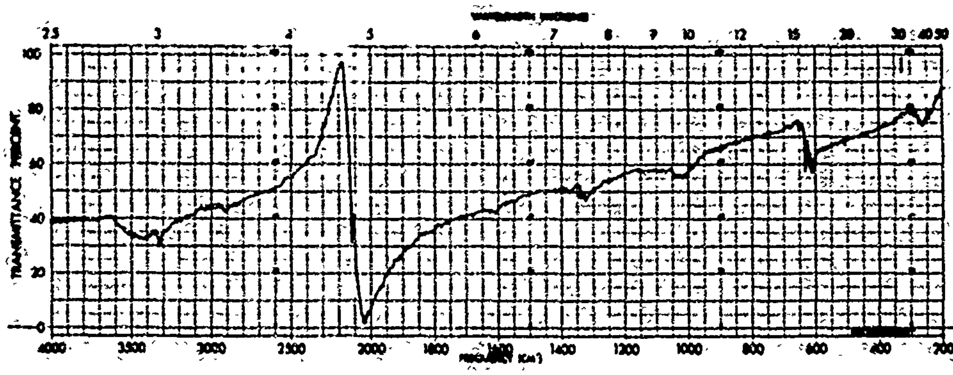
Spectrum	Code
21. Potassium perchlorate	Oxidizer 9
22. Barium chromate	Oxidizer 10
23. Lead chromate	Oxidizer 11
24. Barium peroxide	Oxidizer 12
25. Strontium peroxide	Oxidizer 13
26. Lead monoxide	Oxidizer 14
27. Red lead (Pb_3O_4)	Oxidizer 15
28. Ferric oxide	Oxidizer 16
29. Molybdenum trioxide	Oxidizer 17
30. Dechlorane (perchloropentacyclodecane)	Color Intensifier 1
31. Sodium oxalate	Color Intensifier 2
32. Strontium oxalate	Color Intensifier 3
33. Gum arabic	Binder 1
34. Polyvinyl chloride	Binder 2
35. Parlon (chlorinated rubber)	Binder 3
36. Stearic acid	Binder 4
37. Wax	Binder 5
38. Calcium resinate	Binder 6
39. Ethyl cellulose	Binder 7
40. Oxamide	Misc. 1

Table I. Identification of Spectra (cont'd)

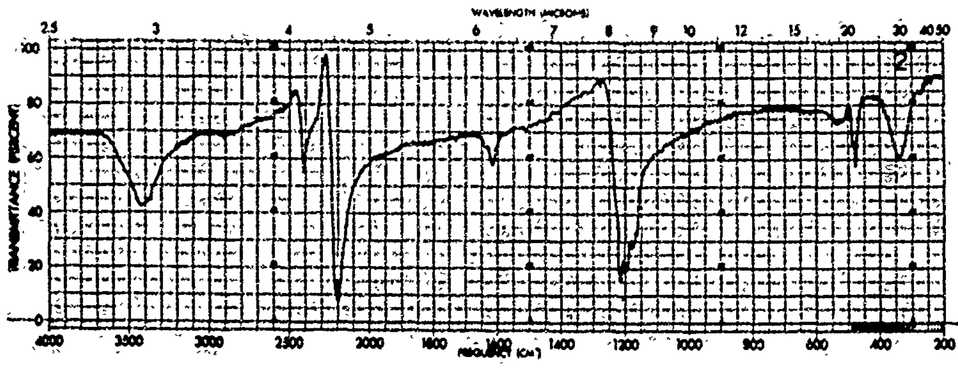
Spectrum	Code
41. Barium monoxide	Misc. 2
42. Lead thiocyanate	Misc. 3
43. Calcium carbonate	Misc. 4
44. Detonator	Mix 1
45. Igniter	Mix 2
46. Primer	Mix 3
47. Primer	Mix 4
48. Primer	Mix 5
49. Detonator	Mix 6
50. Detonator	Mix 7

Table II: Analysis of Typical Compositions

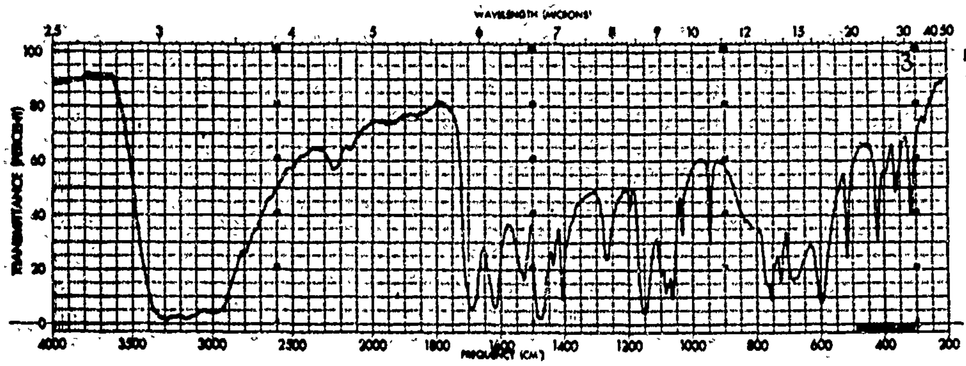
Spectrum	Infrared	Emission Spectroscopy	Combined Analysis
44	RDX TNT		RDX TNT
45	$BaCrO_4$ Pb_3O_4	Pb, Cr, Ba, Zr	$BaCrO_4$ Pb_3O_4 Zr
46	Hg Fulminate $KClO_3$	K, Sb, Hg	Hg Fulminate $KClO_3$ Sb_2S_3
47	Hg Fulminate $KClO_3$ $Ba(NO_3)_2$	K, Ba, Sb, Hg	Hg Fulminate $KClO_3$ $Ba(NO_3)_2$ Sb_2S_3
48	Normal Pb Styphnate PETN $Ba(NO_3)_2$	Al, Sb, Pb, Ba	Normal Pb Styphnate PETN $Ba(NO_3)_2$ Al Sb_2S_3
49	Pb Azide PETN	Pb	Pb Azide PETN
50	RDX Stearic Acid		RDX Stearic Acid



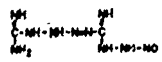
Primary Explosive 1
Lead azide
$Pb(N_3)_2$

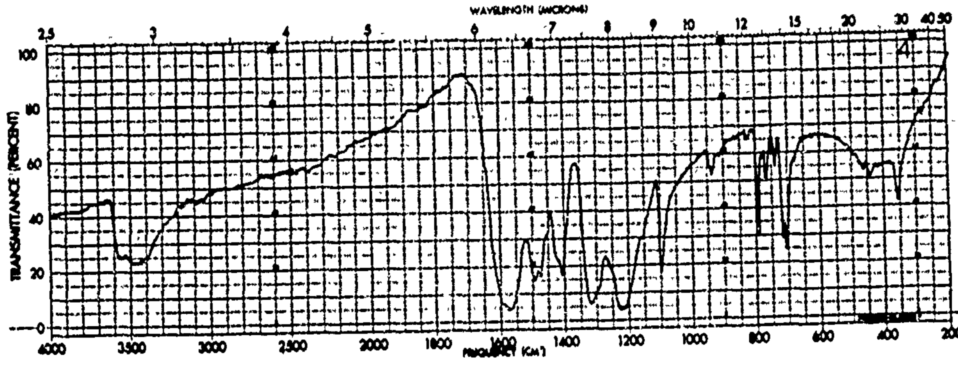


Primary Explosive 2
Mercury fulminate
$Hg(ONC)_2$

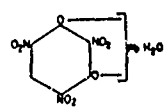


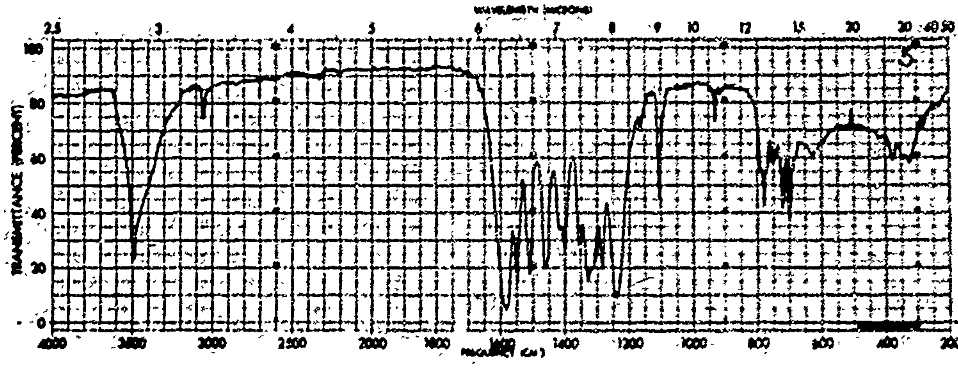
Primary Explosive 3
Tetracene



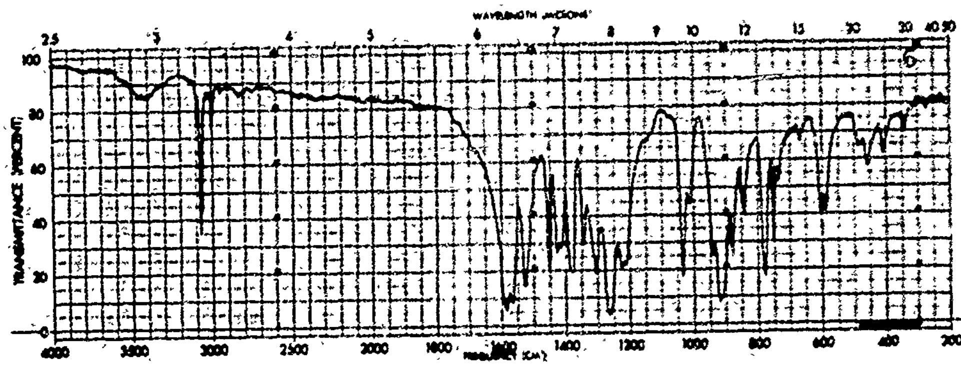


Primary Explosive 4
Normal lead styphnate

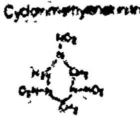


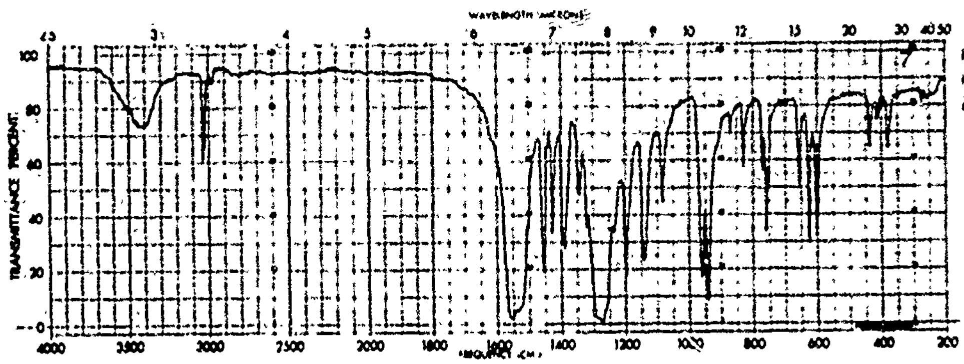


Primary Explosive 5
Basic lead styphnate

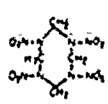


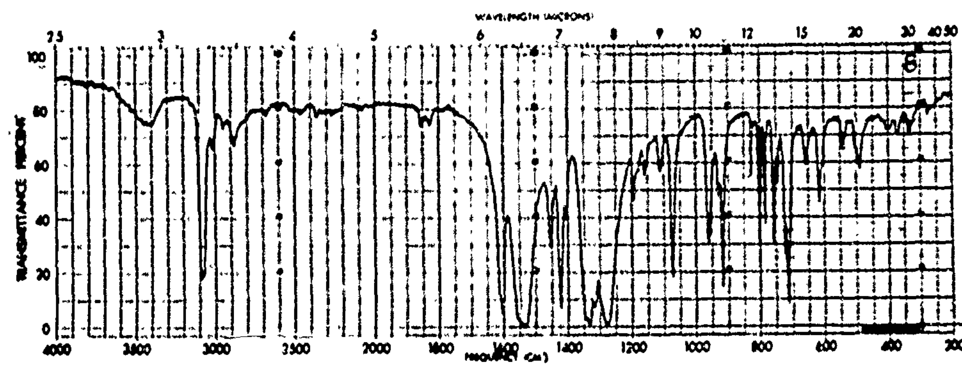
High Explosive 1
RDX (Cyclonite,
Cyclotrimethylenetrinitramine)



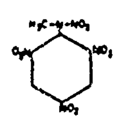


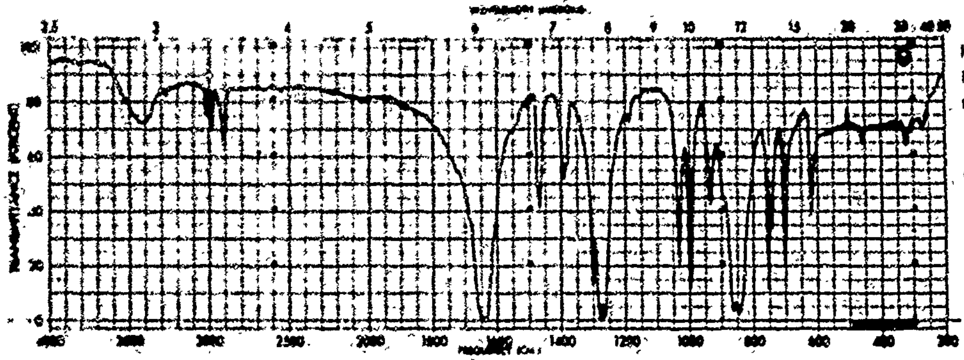
High Explosive 2
HMX (Cyclotetra-
methylenetetranitramine)



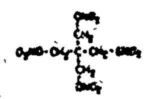


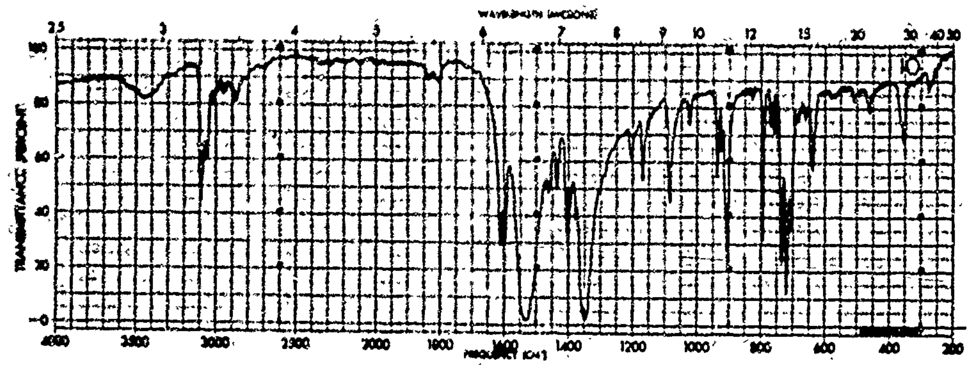
High Explosive 3
Tetryl (2,4,6-Trinitro-
phenylmethylnitramine)



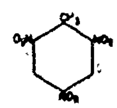


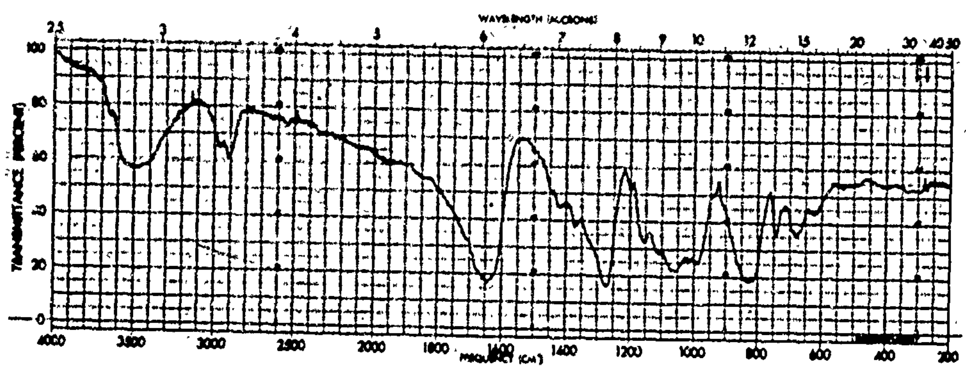
High Explosive 4
PETN (Pentaerythritol tetranitrate)





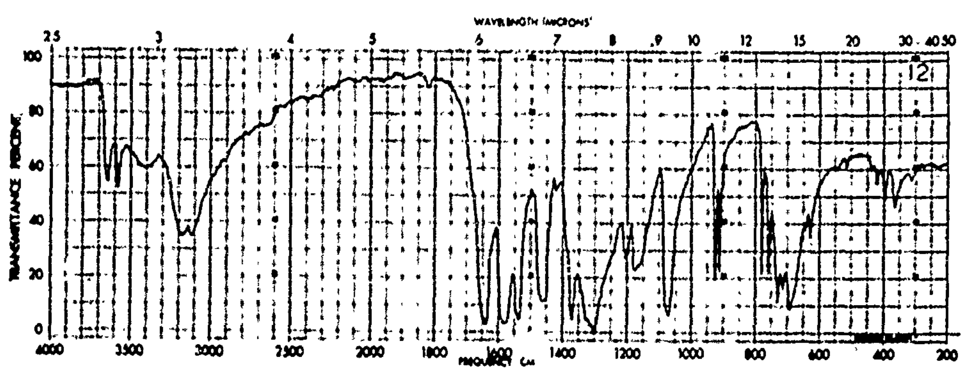
High Explosive 5
TNT (2,4,6-Trinitrotoluene)



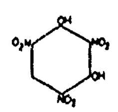


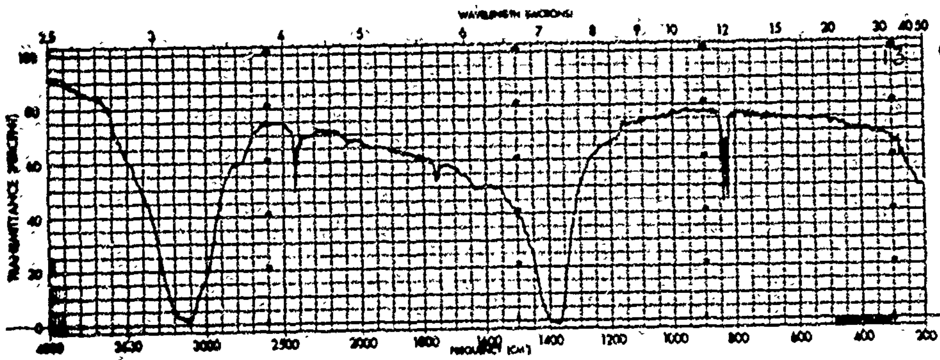
High Explosive 6
Nitrocellulose

$[C_6H_7O_5(NO_2)_3]_x$

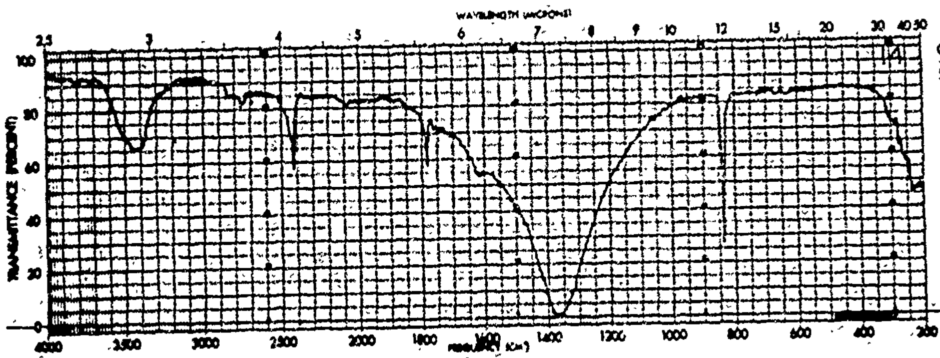


High Explosive 7
Styphnic Acid
(2,4,6-Trinitroresorcinol)

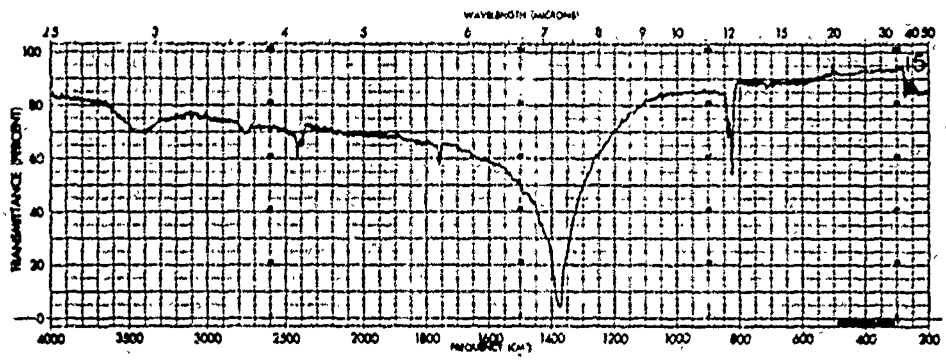




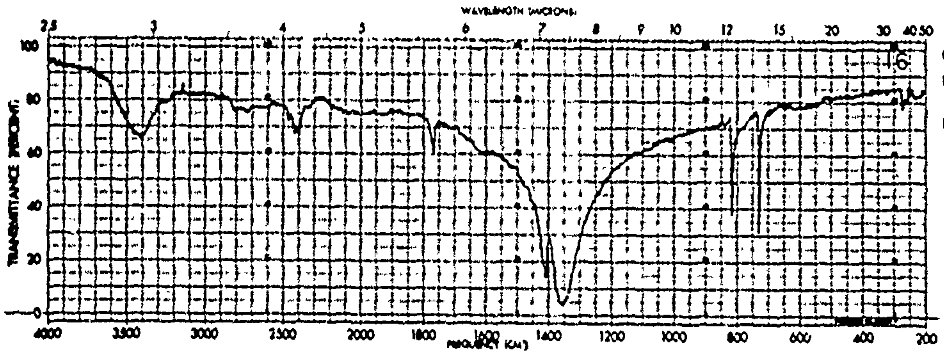
Oxidizer 1
Ammonium Nitrate
NH_4NO_3



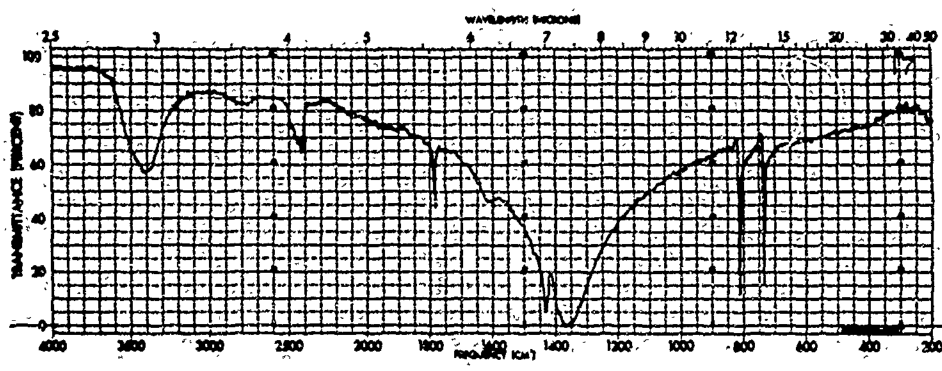
Oxidizer 2
Sodium Nitrate
$NaNO_3$



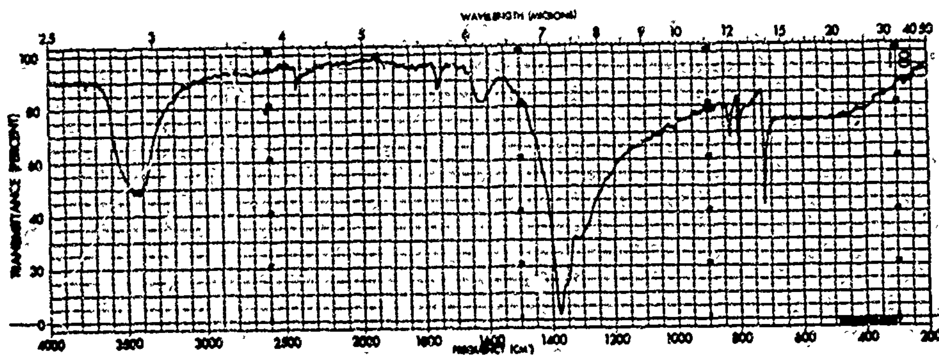
Oxidizer 3
Potassium Nitrate
KNO_3



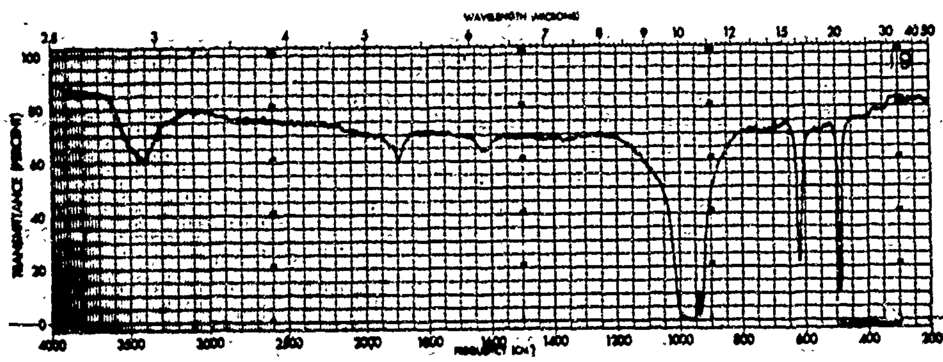
Oxidizer 4
Barium Nitrate
$Ba(NO_3)_2$



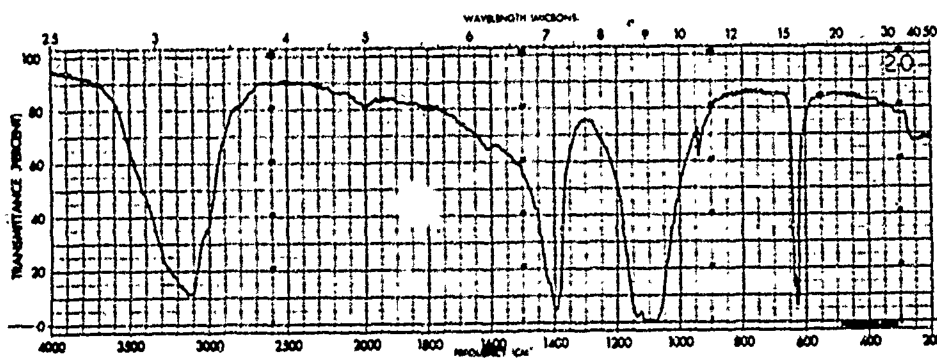
Oxidizer 5
Strontium Nitrate
$Sr(NO_3)_2$



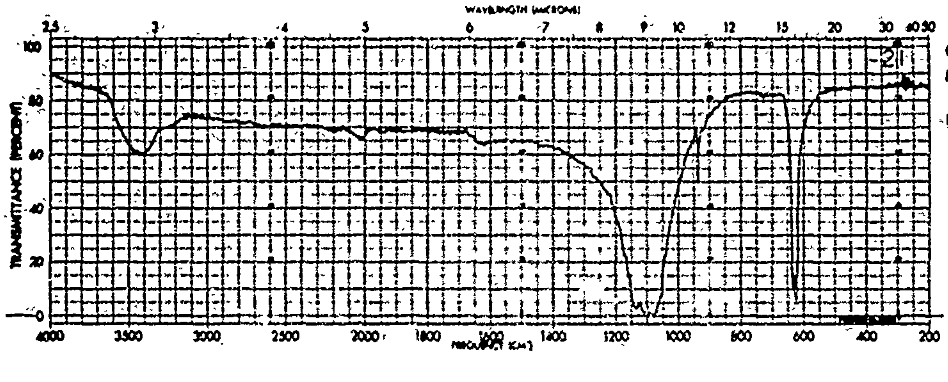
Oxidizer 6
Lead Nitrate
$Pb(NO_3)_2$



Oxidizer 7
Potassium chlorate
$KClO_3$

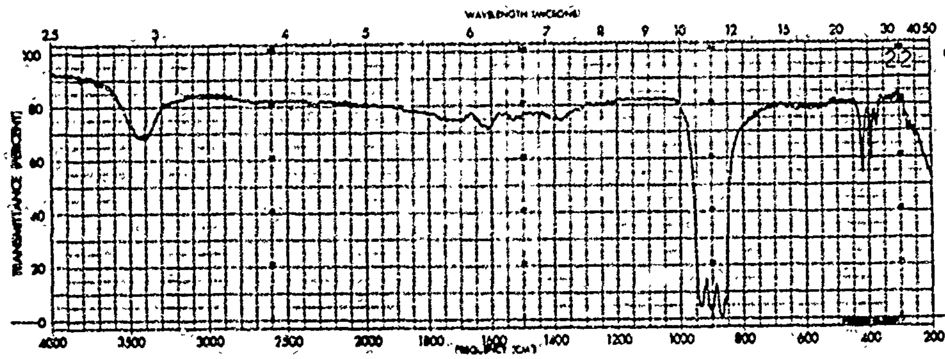


Oxidizer 8
Ammonium perchlorate
NH_4ClO_4



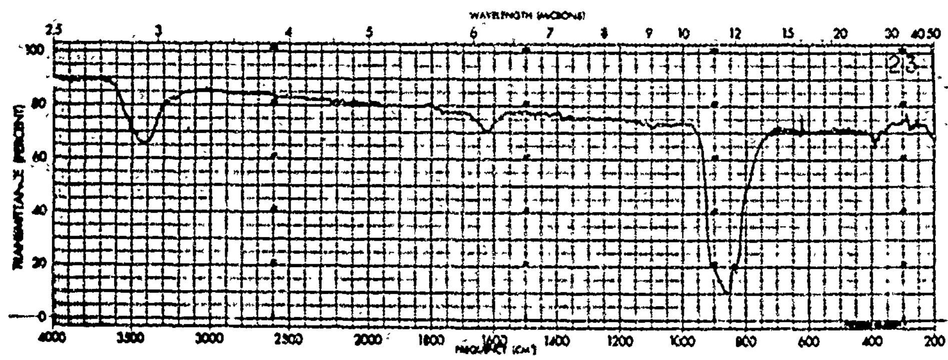
Oxidizer 9
Potassium perchlorate

$KClO_4$



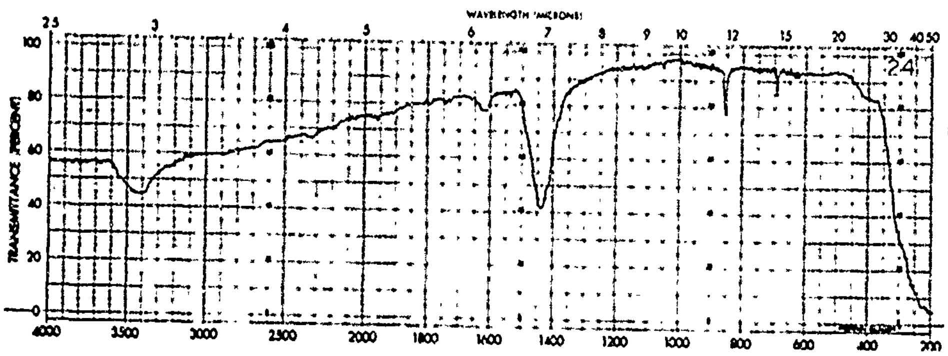
Oxidizer 10
Barium chromate

$BaCrO_4$



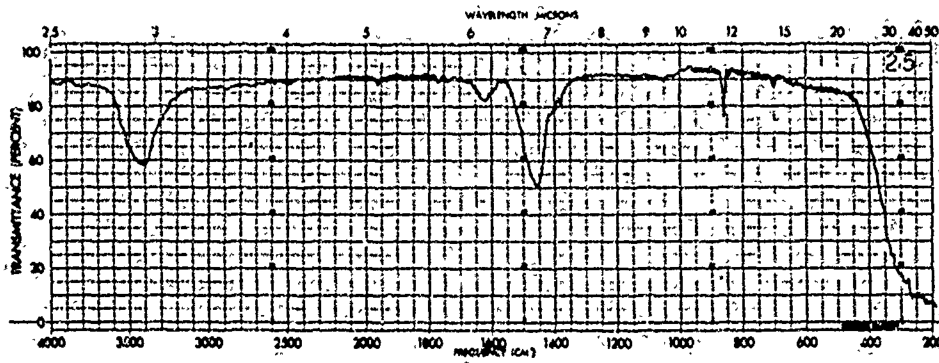
Oxidizer 11
Lead chromate

$PbCrO_4$



Oxidizer 12
Barium peroxide

BaO_2



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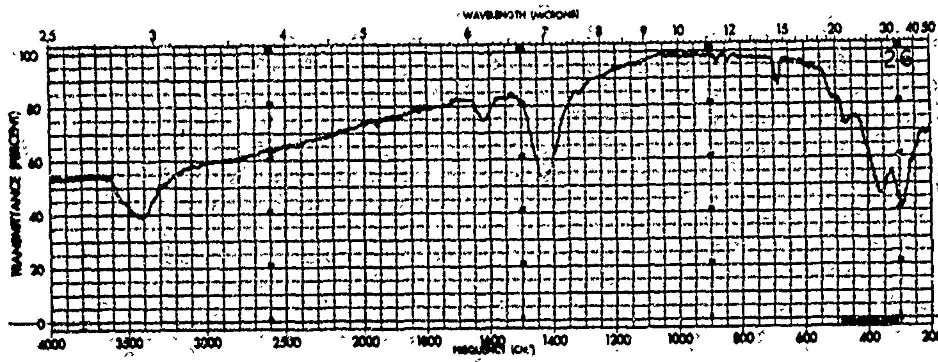
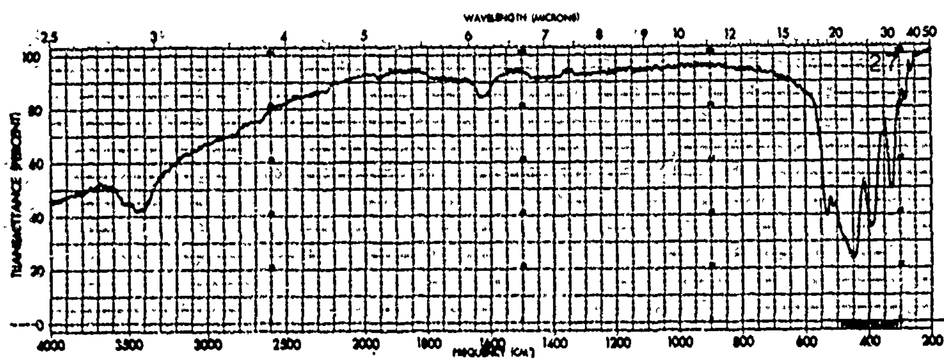
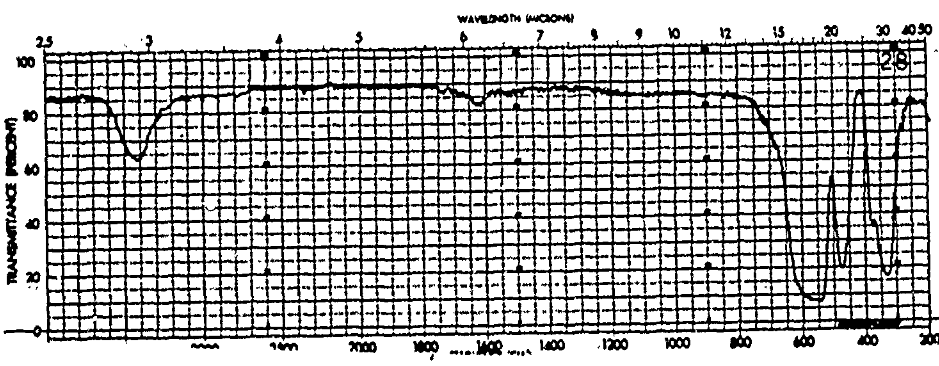
Strontium peroxide
SrO_2



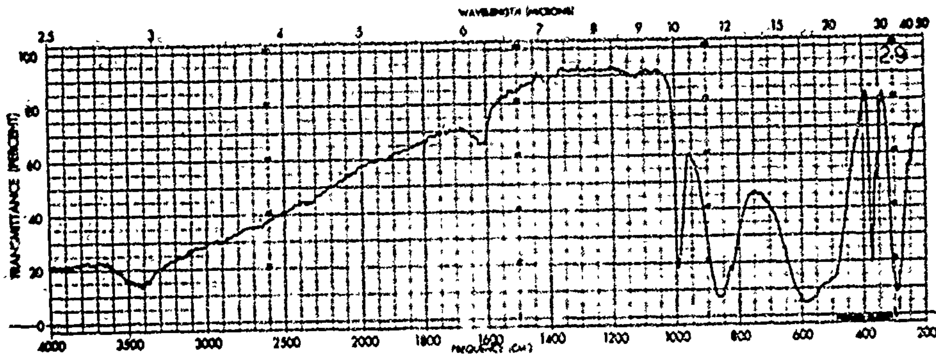
Oxidizer 14
Lead monoxide
PbO



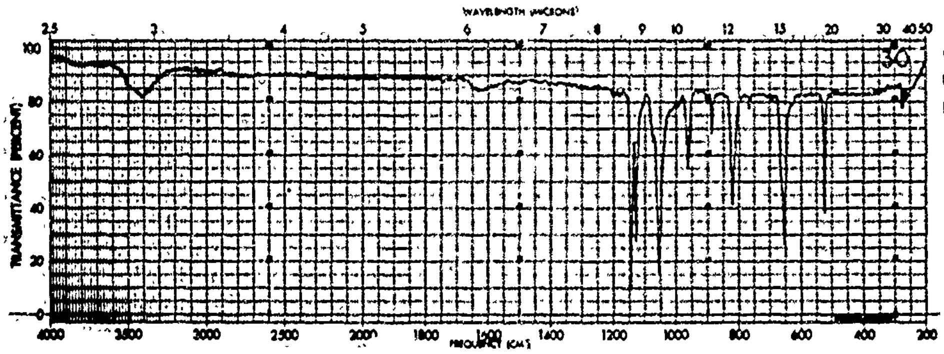
Oxidizer 15
Red lead
Pb_3O_4



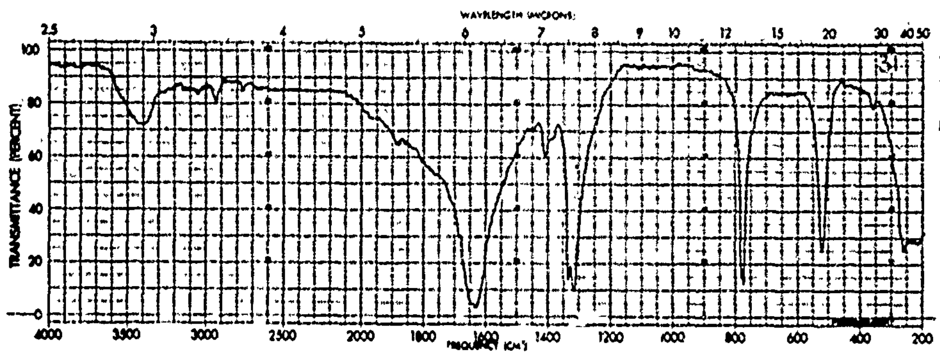
Oxidizer 16
Ferric oxide
Fe_2O_3



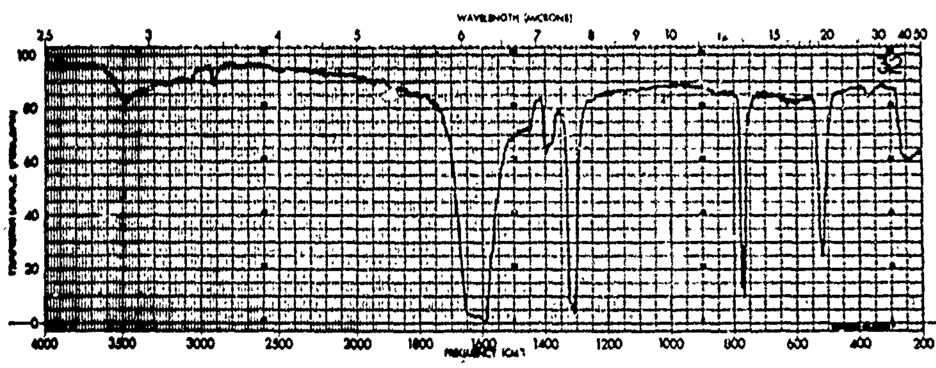
Oxidizer 17
Molybdenum trioxide
MoO_3



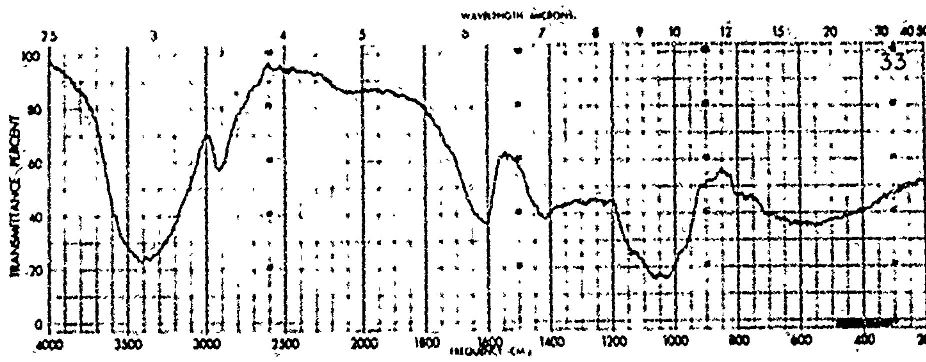
Color Intensifier 1
Dechlorane (Perchloro-pentacyclodecane)



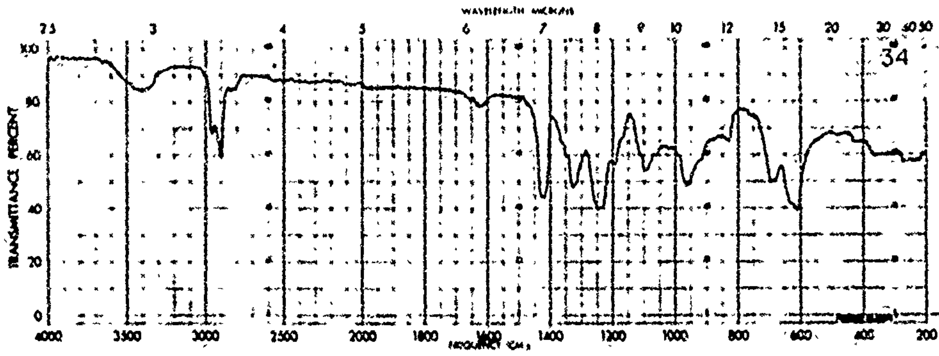
Color Intensifier 2
Sodium oxalate
$Na_2C_2O_4$



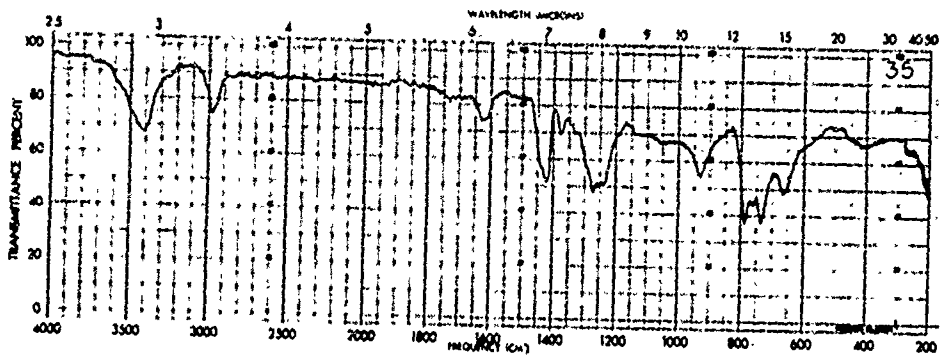
Color Intensifier 3
Strontium oxalate
SrC_2O_4



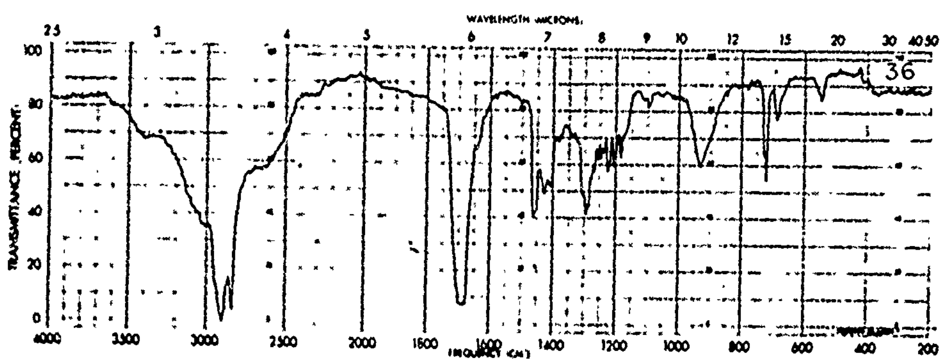
Binder 1
Gum arabic



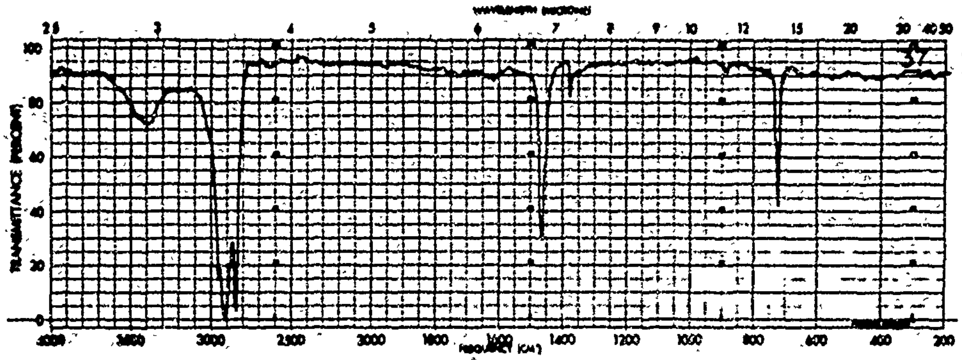
Binder 2
PVC (Polyvinylchloride)



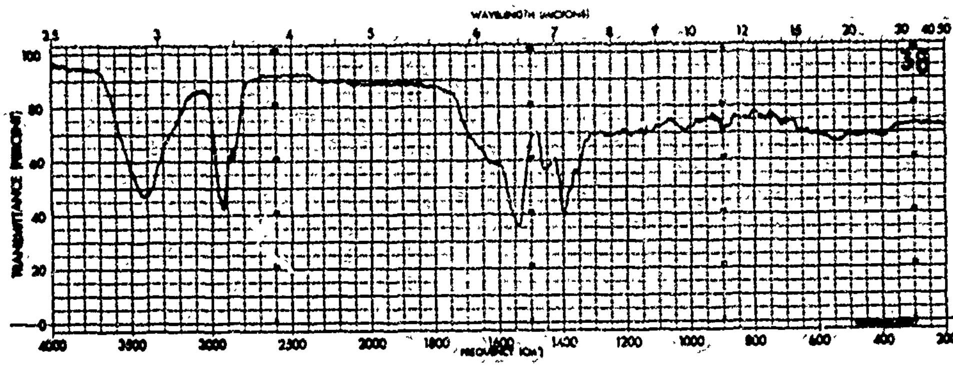
Binder 3
Parlon (Chlorinated rubber)



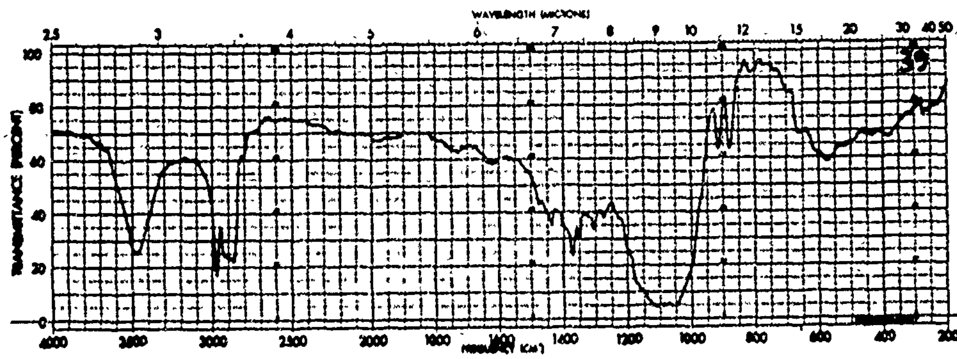
Binder 4
Stearic acid
$CH_3(CH_2)_{16}COOH$



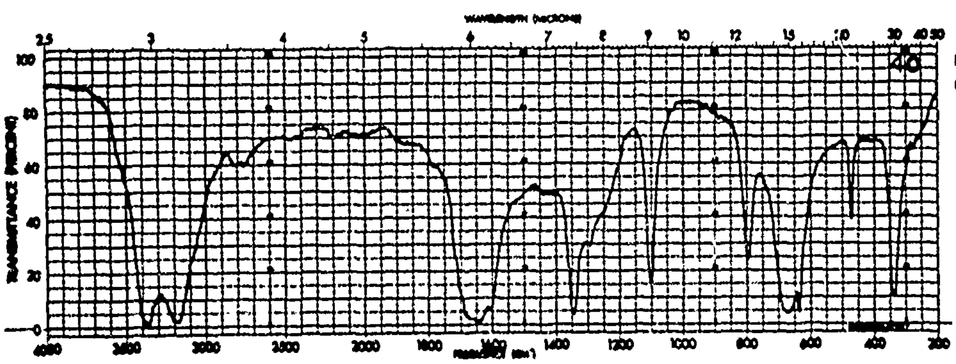
Binder 5
Wax



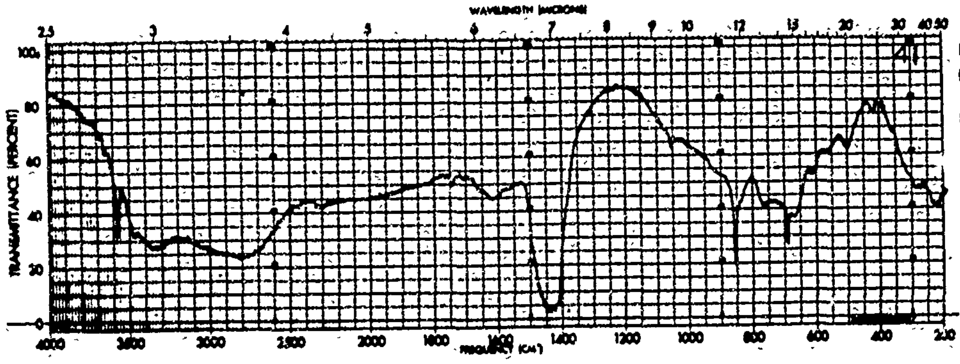
Binder 6
Calcium resinate



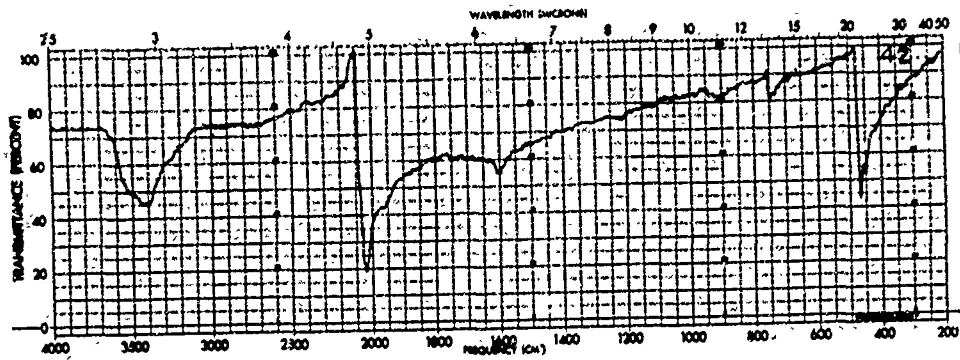
Binder 7
Ethyl cellulose
$[C_6H_7O_2(C_2H_5)_3]_x$



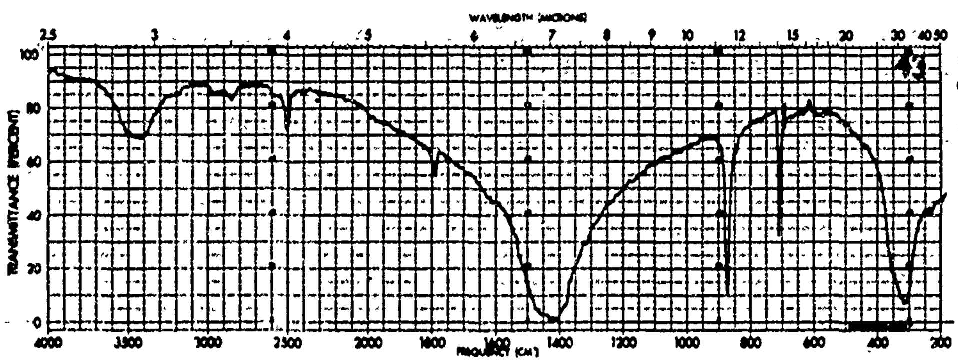
Misc. 1
Oxamide
$CONH_2$
$CONH_2$



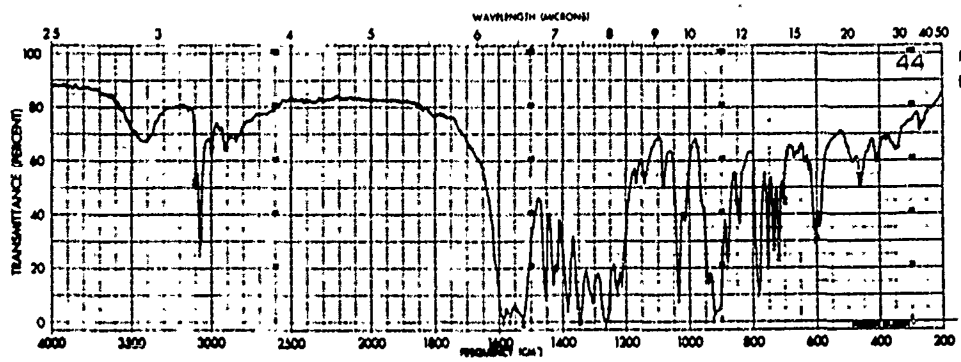
Misc. 2
Barium monoxide
BaO



Misc. 3
Lead thiocyanate
$Pb(SCN)_2$

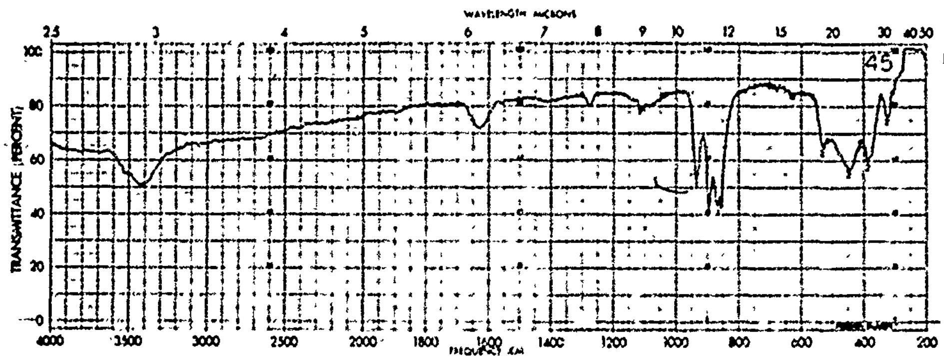


Misc. 4
Calcium carbonate
$CaCO_3$

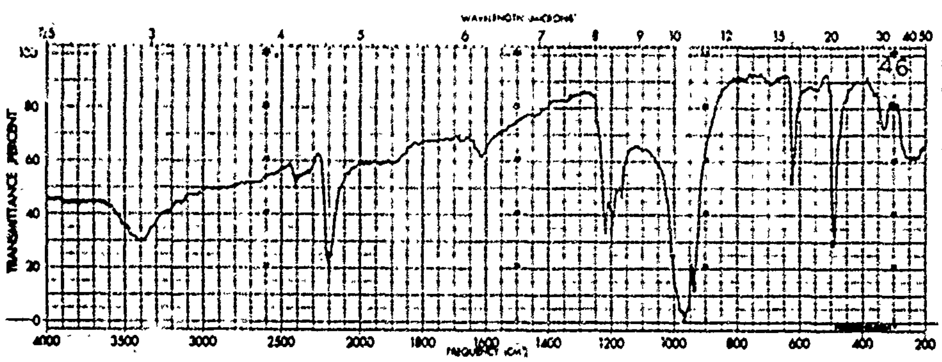


Mix 1
Detonator

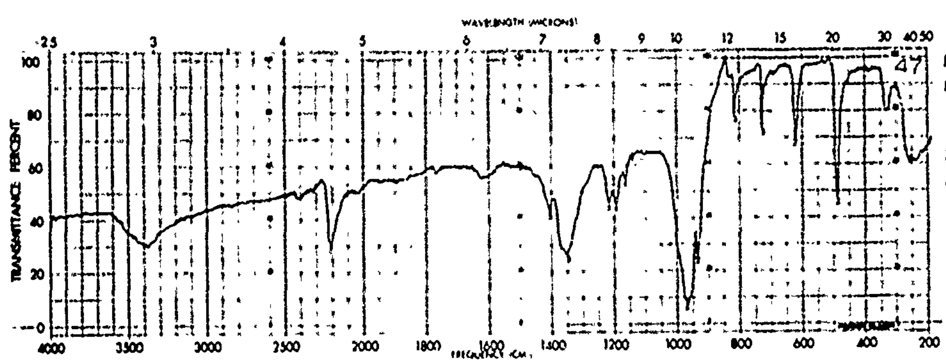
1. RDX
2. TNT



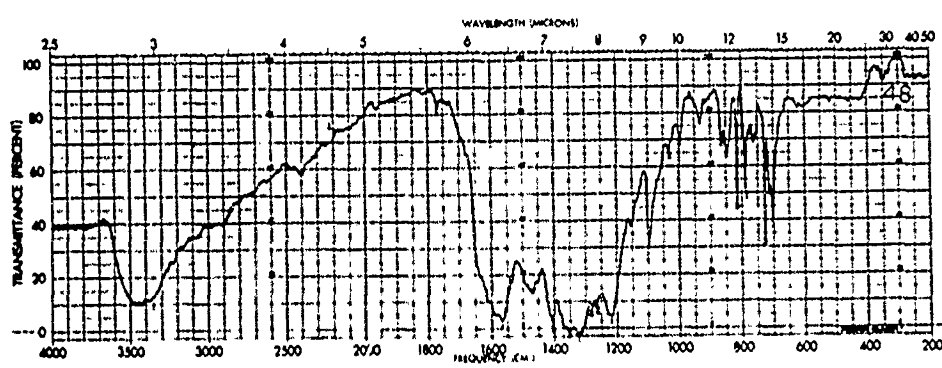
Mix 2
Igniter
1 $BaCrO_4$
2 Pb_3O_4



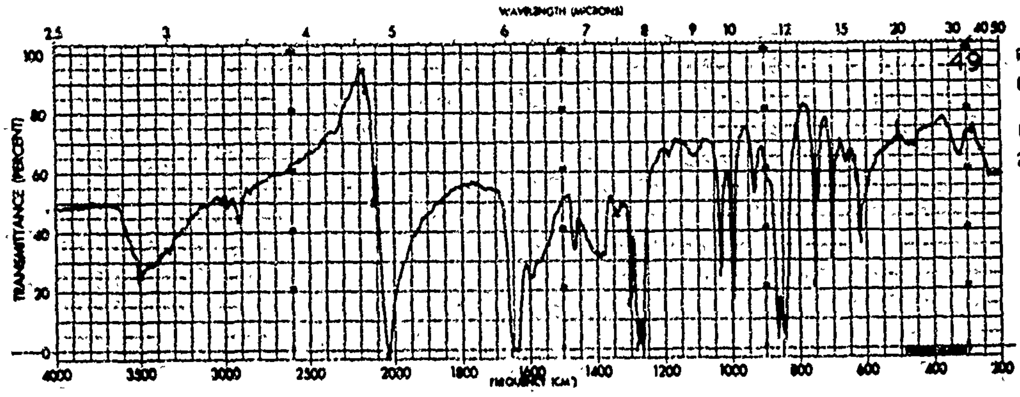
Mix 3
Primer
1 Mercury fulminate
2 $KClO_3$



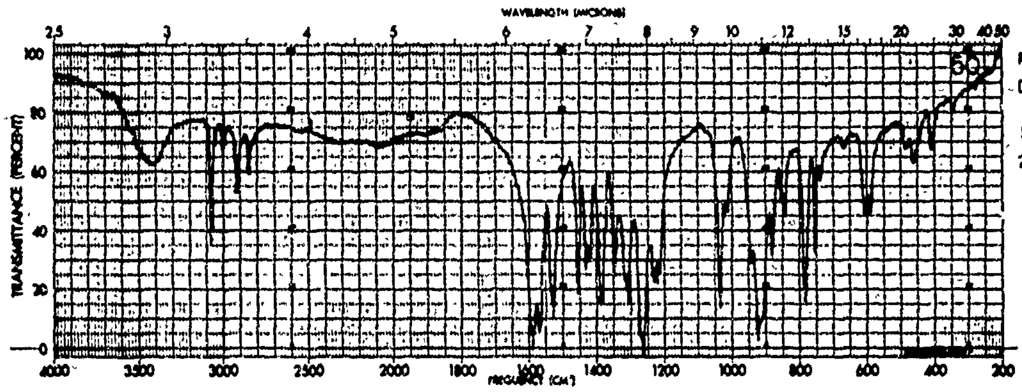
Mix 4
Primer
1. Mercury fulminate
2 $KClO_3$
3 $Ba(NO_3)_2$



Mix 5
Primer
1 Normal lead styphnate
2 PETN
3 $Ba(NO_3)_2$



Mix 6
Detonator
1. PETN
2. Lead azide



Mix 7
Detonator
1. RDX
2. Stearic acid